

Research Article

Effect of Acetylation Method on Characterization of Cellulose Acetate based Sago “hampas”

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ABSTRACT

Sago waste is a potential source of cellulose but it has not been utilized properly. To improve the properties of cellulose based sago waste, it can be done by acetylation process. The objective of this research was to create cellulose acetate from sago waste with variation of acetic anhydride concentration. Microcrystalline cellulose could be prepared from sago waste resulted in yield around 43% with 59% cellulose content. Acetylation process was done to microcrystalline cellulose from sago waste. FTIR profiling showed that the replacement of the acetyl groups on hydroxyl groups was done with acetate anhydride addition. Acetate anhydride concentration was affected yield, acetyl group and degree of substitution. The suitable acetic anhydride volume of acetylation process was 66 ml produced cellulose acetate with yield 85.33%, degree substitution 2.16, and acetyl content 36.87%.

Keywords: sago waste, cellulose acetate, Acetate anhydride

INTRODUCTION

Cellulose is the most abundant polysaccharides on earth. It is an important structural component of plants, many forms of algae, and oomycetes [1]. Because of its biodegradability and chemical stability, cellulose has been used for more than 150 years for paper, pharmaceutical compounds, and textiles [2]. In recent years, scientists also have been trying to maximize its potential as packaging materials. However, the application of this cellulose-based packaging is still not widely used. Several problems regarding its poor mechanical and barrier properties still need to be solved by chemical and physical treatment [3]. One of the chemical treatment that has been

widely used is acetylation to improve cellulose compatibility and dispersion on solvent [4].

Sago is a native plant of South East Asia. Around 50% of the world sago plants grow in Indonesia [5] and 90% of that number grows in Papua and Maluku Province of Indonesia [6]. The commercial utilization of sago plant only focused on the extraction of its starch with yield only around 18.8 – 38.8% [7], whereas the waste can be processed to other products. The utilization of sago waste or ‘hampas’ has been reported to produce biethanol [8], as biomass source to produce biohydrogen [23] and oil spill removal [24]. Sago ‘hampas’ is a lignocellulosic

by-product produced from sago palm pith after starch extraction. Sago ‘hampas’ contains cellulose which has potentially as material to produce bioplastic and other products. Cellulose fibers have relatively high strength, high stiffness, and low density but insoluble in organic or inorganic solvent, so it has limitation to utilize cellulose as material of product like bioplastic. To improve cellulose solubility, it can be done by acetylation. Solubility of cellulose acetate was influenced by degree of substitution. A study on the synthesis of cellulose acetate based on sago ‘hampas’ has not been done. This research was studied about effect of acetate anhydride concentration on cellulose acetate based sago ‘hampas’ characteristics..

MATERIALS AND METHOD

MATERIALS

The sago ‘hampas’ was obtained from local farmer in Sorong Selatan, West Papua. Chemical reagents p.a. qualified NaOH, HCl, NaOCl, acetic acid glacial, H₂SO₄, acetate anhydride and aquadest to produce microcrystalline cellulose and acetylation process.

METHODS

Preparation Microcrystalline Cellulose based Sago ‘hampas’

Microcrystalline cellulose based sago ‘hampas’ was conducted following the method obtained from Ahmad *et al.* method [9]. 24 g of dried sago ‘hampas’ were refluxed with 240 mL of 1M NaOH at 80°C for 1h and 36 mins to solubilize the lignin and hemicellulose. Following alkali treatment, the alkaline treated sago waste was washed and filtered until the liquid was clear. The filtrate was then refluxed with 240 mL of 5% sodium hypochlorite (NaOCl) at 80°C for 18 min for the bleaching process. After another washing and filtration step, it then was hydrolyzed with 122 mL of 2 M HCl at room temperature for 30 min under continuous stirring. It was repeatedly washed with distilled water until pH seven is achieved. The cellulose was dried in an oven at 50°C for 24h. The mass of dried cellulose was recorded to

calculate the yield, water content, and cellulose content.

Cellulose Acetate Synthesis

Cellulose acetate synthesis was conducted following Bahmid *et al.* method [10] with some modification. 10 gram of cellulose based sago ‘hampas’ and 100 ml glacial acetic acid were mixed and stirred at 38°C for one hour. The mixture was added by 2 ml of H₂SO₄ and was stirred for 45 min at 38°C. The variation volume of acetic anhydride 0, 30, 60 and 66 ml were added to the mixture, and the mixture were continuously stirred at 38°C for one hour. After that, 25 ml of distilled water and 50 ml of glacial acetic acid were added in several portions for 30 minutes under stirring. The mixture was washed with distilled water until the liquid became clear using centrifugation at 1500 rpm for 15 minutes for each washing. The sediment then was dried at 50°C for 48 hours and grounded and sieved using 50 mesh sieve.

Characterization of Cellulose Acetate

Cellulose acetate was measured its yield, water content, degree of acetylation, and the characteristic of the profile. Yield was calculated by the weight recorded before and after the treatment. Water content was measured using AOAC method [11]. FTIR spectra profil analysis using Shimadzu IR Prestige 21 on scanning range 400 to 4000 nm was done to obtain the profile of the materials.

Determination of acetyl content was followed based on Candido and Gonçalves method [12]. 0.1 g cellulose acetate was soaked with 5 ml of 0.25 NaOH and 5 ml of ethanol for 24 h. Following the soaking, 10 ml of 0.25 M HCl was added into the mixture and was left for 30 min. This mixture was then titrated by a standard 0.25 M NaOH solution, using phenolphthalein as indicator. The percentage of acetyl groups (%AG) was calculated by following equation:

$$\%AG = \{[(V_{bi} + V_{bt}) * \mu_b - (V_a * \mu_a)] * M * 100\} / m_{ac}$$

Where:

V_{bi}: volume of NaOH added to the system (L)

V_{bt}: volume of NaOH spent in titration (L)

μ_b: NaOH concentration (M)

Va: volume of HCl added to the system (L)

μ a: HCl concentration (M)

M: molar weight of acetyl group (43 g/mol)

mac: weight of cellulose acetate sample (g)

Meanwhile, the degree of substitution was calculated using following equation from Elomaa *et al.* [13].

$$DS = 162 * \%AG / [4300 - (42 * \%AG)]$$

RESULTS AND DISCUSSION

Microcrystalline Cellulose based Sago ‘hampas’

Characteristics of dried sago ‘hampas’ and microcrystalline cellulose based sago ‘hampas’ can be seen from Table 1.

Table 1. Characteristics of sago ‘hampas’ and microcrystalline cellulose based sago ‘hampas’

	Water content (% db)	Cellulose content (%)	Yield (%)
Sago waste	16.38±0.84	35.47±0.17	-
MCC	11.29±0.08	58.83±0.12	42.91±1.12

From the result, it shows that sago ‘hampas’ still has relatively high cellulose content, around 35%. The remaining composition of that could be the starch, hemicellulose, and lignin. Sago waste or hampas contains 58% starch, 23% cellulose, 9.2% hemicellulose, and 4% lignin [14]. According to Chew and Shim [15], microscopic examination showed that a large amount of starch granules were trapped within the lignocellulosic matrix of sago waste. The relatively high cellulose content on this experiment most likely caused by soaking as pretreatment which was done before the cellulose extraction. Some amount of starch which is a soluble carbohydrate were already dissolved in the soaking process, making the sago waste cellulose more concentrated.

After the cellulose extraction, the cellulose content increased to approximately 59%. The alkali treatment solubilized lignin and

hemicellulose [9]. Since some of other fibers have degraded, the cellulose content increased. The yield of the extraction process was around 43%. The MCC was made by hydrolysis of cellulose on its glycosidic bond [16].

FT-IR spectra of MCC and cellulose acetate based Sago ‘hampas’

Figure 1 showed FT-IR spectrum of cellulose acetate produced by various volume of acetic anhydride. There are cellulose-specific groups in standard cellulose (-OH, -CH₂, -O- groups) that appear repeatedly. The -OH group appears at wave number 3348,42 cm⁻¹, while wave number 2900,94 cm⁻¹ shows vibration CH₂ which is the main frame builder of cellulose compound reinforced with vibration at wave number 2366,59 cm⁻¹. The -O- group that assembles cellulose appears at wave numbers 1319.31 and 1373.32 cm⁻¹ [25]. The absence of vibration in the wave number 1509-1609 cm⁻¹ and 1700-1740 cm⁻¹ on the FT-IR cellulose spectral profile of MCC showed no presence of lignin and hemicellulose compounds in the MCC based sago ‘hampas’ [26]. From Fig 1, It can be seen that there is an alteration of intensity band at ~3400 cm⁻¹. On the control, the intensity is around 4.3%T, while the cellulose acetate had the intensity of peak around 12.9%T. This conversion means that there is a modification of hydroxyl groups to acetyl groups [12]. On Figure 1, it was also shown an adsorption peak at 1242 cm⁻¹ which assigned for C-O stretching of acetyl group, which wasn’t observed on MCC sago waste and treatment 0 ml acetic anhydride [17]. The strong intensity band presented at 1751 cm⁻¹ of acetic anhydride addition is assigned to symmetric carbonyl group (C=O) of acetyl group [18]. This figure confirm that there wasn’t acetic acid and acetate anhydride residue by the absence of band at 1760-1840 cm⁻¹ [19]. There is a noticeable peak at 902 cm⁻¹ of cellulose acetate which indicated the degradation of cellulose due to acetylation process [20].

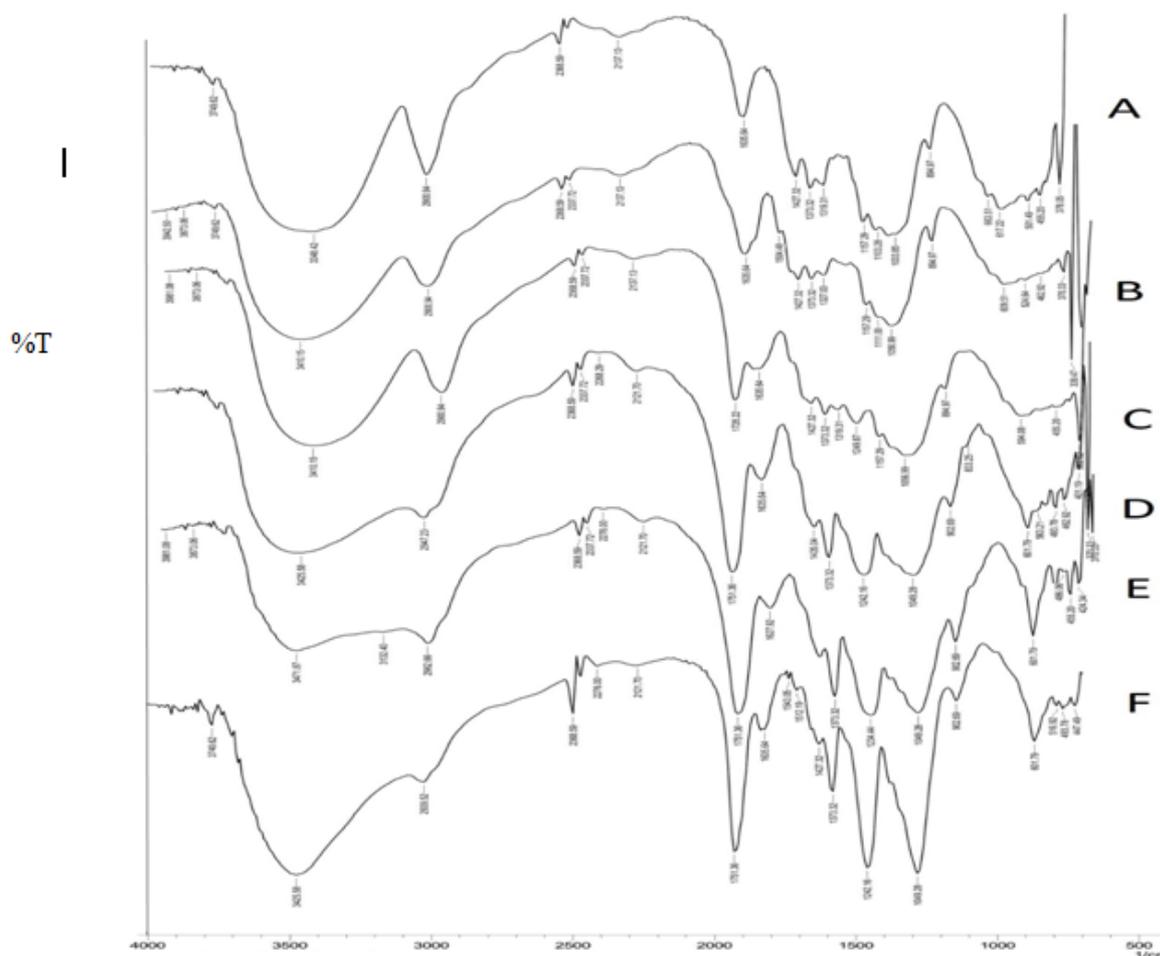


Fig 1. FT-IR spectra of cellulose standard (A); MCC sago ‘hampas’ (B); cellulose acetate treatment 0 ml acetate anhydride (C); 30 ml acetate anhydride (D); 60 ml acetate anhydride (E); 66 ml acetate anhydride (F)

Characteristic of cellulose acetate

Cellulose acetate was produced in several stages namely activation, acetylation, hydrolysis, sedimentation and drying. Before the acetylation process, the activation process was done to expand the surface area of cellulose fibers [10] and to disrupt the intra and intermolecular hydrogen bonds, and degrades the crystalline regions of fiber, raising the accessibility to the OH groups for acetyl substitution [12]. Activation was done by using glacial acetic acid as activator and sulfate acid as catalyst. There were some trials done using different volume of acetic anhydride. The result was given at Table 2.

Table 2. Characteristics of cellulose acetate produced by different volume of acetate anhydride

Acetic Anhydride Added (ml)	Water content (% db)	Yield (%)	Acetyl Groups (%)	Degree of Substitution
0 ml	4.46 ^a	76.46 ^a	8,49 ^a	0,89 ^a
30 ml	8.46 ^b	81.89 ^a	33,74 ^b	1,90 ^b
60 ml	13.46 ^c	85.33 ^{ab}	36,56 ^c	2,14 ^b
66 ml	15.65 ^c	90,05 ^b	36,87 ^c	2,17 ^b

Means of triplicate determination \pm S.D. with the same letter in a column within each property are not significantly different ($p < 0.05$)

Water content of the cellulose acetate appeared to increase with the addition of acetic anhydride. This might be caused by release of

OH groups to the environment as a result from acetyl groups substitution. Those OH groups formed free water molecules and thus increased

the water content of the materials. The yield was also increased proportionally to water content. This is might be due to water molecules will add more weight to the material itself. The more acetic anhydride used for acetylation, the more acetyl groups formed on the cellulose, but the increase was not linear, since acetylation as chemical reaction process also depends on some other factors like the availability of substrate, the efficiency of the reactant, surface contact, etc.

Fischer *et al.* [21] used cellulose acetate with DS between 2 to 2.5 to see the solubility in several organic solvents. Barud *et al.*[17] managed to produce cellulose acetate within range 2.30 to 2.77. Candido *et al.*, [12] succeeded in obtaining cellulose acetate with DS 2.72. Meanwhile Bahmidet *al.* [10] produced cellulose acetate with DS ranging between 2.3 to 2.8 to be used as source material for nanocellulose acetate production on electrospinner. Treatment of acetate anhydride addition on acetylation process affect the degree of substitution and acetyl content of cellulose acetate. More acetate anhydride were added, more acetyl content and the degree of substitution of cellulose acetate. Acetylation by using only glacial acetic acid produce cellulose acetate with low DS. It might be due to glacial acetic acid just play in role of activation only, it was not sufficient to destroy the hydrogen bonds [18]. Acetylation process using 60 ml acetic anhydride is suitable which resulted on 36,56% acetyl group which has high degree of substitution (DS) 2.14. Therefore, acetic anhydride has a good accesibility to destroy the hydroxyl groups of cellulose.

Based on Kamide *et al.* [22], cellulose acetate with DS between 0.39 and 0.81 is soluble in water. The polymer with DS 0.49 is insoluble in less polar solvents such as hydrocarbons, chlorinated hydrocarbons, amines, and esters. Cellulose acetate is soluble in very polar organic solvent such as formic acid, trifluoroacetic acid, dimethylacetamide, dimethyl sulfoxide, water, and formamide. The solubility of it is controlled primarily by the dielectric constant of the solvent.

CONCLUSION

Sago waste is a potential source for the cellulosic material since it contains relatively high cellulose. Cellulose conversion to Cellulose acetate can be produced by acetate anhydride addition. The effectiveness of the acetylation depends also on the concentration of acetate anhydride. FTIR profiling showed that cellulose based sago waste conversion to CA is clearly confirmed through formation of strong intensity bands at 1751, 1242 and 902 cm^{-1} . In addition, the results of FT-IR analysis indicated that there is no free acetic acid and/or acetic anhydride residue. The suitable acetylation process is treatment of 66 ml acetate anhydride which produced cellulose acetate with yield 85.33%, degree substitution 2.16, and acetyl content 36.87%.

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